Raw milk quality – Part 2. Milk

chemical components and

nutritional properties of milk



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Cow milk composition [%]

(according to Walstra et al. 2009)

Component	Average content	Range
Water	87.1	85.3 - 88.7
Dry matter	12.9	11.3 – 14.7
Fat	4.0	2.5 – 5.5
Total protein	3.25	2.3 – 4.4
Lactose	4.6	3.8 – 5.3
Ash	0.7	0.57 – 0.83
Organic acids	0.17	0.12-0.21
Miscellaneous	0.15	



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Milk fat

0.3 – 1.6 %

0.2 - 1.0%

0.01 - 0.07 %

<u>Simple/neutral lipids (esters of alcohol and FA):</u> 96 - 99 % of total fat content

- Triglycerides
- Diglycerides
- Monoglycerides 0.002 0.1 %
- <u>Complex lipids:</u>
 - Phospholipids*
 - Cerebrosides
- **Derivatives:**
 - Free fatty acids 0.1 0.4 %
- Other minor components:
 - Sterols**
 - Carotenoids
 - Vitamin A
 - Vitamin D
 - Vitamin E
 - Vitamin K

0.2 - 0.4% $6 - 10 \mu g/g$ fat

- $6 20 \mu g/g$
- traces
- $5 100 \mu g/g$
- $1 \mu g/g$

* lecithin, sphingomyelin, cephalin, phosphatidylinositide ** cholesteol and its esters



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Milk fat – fatty acids (FA)

	FA type	FA name	Number of C atoms: number of double bonds	%
	Short-chain* and	Butyric*	4:0	2.79
	medium-chain**	Caproic**	6:0	2.34
	(SCFA, MCFA)	Caprylic**	8:0	1.06
		Capric**	10:0	3.04
Saturated (SFA)	Long-chain (LCFA)	Lauric	12:0	2.87
(STA)	Myristic	14:0	8.94	
	Palmitic	16:0	23.80	
		Stearic	18:0	13.20



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Milk fat – fatty acids (FA)

	FA type	FA name	Number of C atoms: number of double bonds	%
Unsaturated	Mono-unsaturated	Palmitoleic	16:1	1.46
(USFA)	(MUFA)	Oleic	18:1	29.6
	Di- and Poly- unsaturated (PUFA)	Linoleic (LA)	18:2, n-6	2.11
		lpha-linolenic (ALA)	18:3, n-3	0.38
		Arachidonic (ARA)	20:4, n-6	0.14



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FAT GLOBULES

- Milk fat membranes: mainly phospholipids, proteins
- density at 15°C 0.93 g/cm³ (0.92 0,94)
- melting point: 31 42°C
- solidification/crystallization point: 19 24°C
- solidification of all triglicerides: below 42°C
- light refractive index at 40°C: 1.4524 1.4578



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FAT GLOBULES





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MILK PROTEINS

Protein		Content in milk (%)	% of nitrogen substances
Casein		2.50	77
Whey prot	eins	0.58	18
	albumins	0.45	14
	immunoglobulins	0.06	2
proteoses and peptones		0.07	2
Total proteins		3.08	95
Non-protein nitrogen compounds*		0.17	5
Nitrogen compounds in total		3.25	100

*ammonia, urea, creatinine, creatine, uric acid and amino acids, and mere traces in the form of vitamins, enzymes, phospholipids and cerebrosides



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MILK PROTEINS - casein

<u>Casein</u> is present in milk in the form of spherical, strongly porous and hydrated aggregates (25 do 300 nm diameter) called micelles.

Casein fractions and their molar masses:

$lpha_{s1}$ -casein	33 %	23 600 Da
α_{s2} -casein	11 %	25 200 Da
β -casein	33 %	24 000 Da
к-casein	11 %	19 000 Da
γ-casein	4 %	20 500 Da

α_{s1} : α_{s2} : β : γ rate = 3:1:3:1



[Dalgleish et al. 2004]



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MILK PROTEINS – whey proteins

Protein	Content in milk (%)	Content in total milk proteins (%)	Isoelectric point - pH
Albumins:			
eta-lactoglobulin	0.30	7.0 - 12.0	5.3
lpha-lactalbumin	0.11	2.0 - 5.0	4.2 – 4.5
Blood serum albumin	0.04	0.7 - 1.3	4.7
Globulins:			
Immunoglobulins	0.06	1.3 – 2.7	4.6 - 6.0
Proteoses and peptones and other milk proteins	0.10	2.0 - 6.0	



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Endogenous milk enzymes

Milk contains about 70 different endogenous (native) enzymes.

Main sources of native milk enzymes:

- cytoplasm of the milk-secreting cells of the mammary gland,
- fat globule membrane,
- blood serum (e.g. lactoperoxidase, ribonuclease)
- leukocytes (e.g. catalase)

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Endogenous milk enzymes

Native milk enzymes are present:

- in water phase np. catalase, lactoperoxidase, ribonuclease,
- in lipid phase, e.g. xanthin oxidase, alkaline phosphatase,
- associated with casein micelles, e.g. proteolytic and lypolitic enzymes.

Most of the milk enzymes belongs to the class of hydrolases and oxidoreductases but only few to: transferases and lyases.



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Functions of milk enzymes

- Worsening of the milk quality: lipoprotein lipase, proteinases, acid phosphatase and xanthine oxidase;
- Improvement of the milk quality: lactoperoxidase (LPO), sulfhydryl oxidase, superoxide dismutase
- Indicators of the heat treatment efficacy in milk: alcaline phosphatase, lactoperoxidase, catalase, γ -glutamyltransferase
- Indicators of health status: N-acetyl-β-D-glucosaminidase, catalase and acid phosphatase
- Antimicrobial enzymes: lysozyme and LPO
- Source of commercial enzymes: ribonucleases and LPO



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$Lactose - C_{12}H_{22}O_{11}$

• reducing disaccharide composed of D-glucose and D-galactose linked through a β -1,4-glucosidic linkage



Lactose – properties

- Molar mass 342.3 g/mol
- Reducing sugar, is oxidised to lactobionic acid;
- On heating it may isomerize to lactulose (glucose moiety converts to fructose)
- In aqueous solutions lactose exists in two isomeric forms $\alpha-$ and $\beta-$
- It has (D-lactose) an ability to rotate the plane of polarization of a beam of plane polarized light clockwise (dextrorotary, positive rotation values)



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Lactose – properties

- Crystallizes from aqueous solutions as $\alpha\text{-}$ monohydrate and anhydrous $\beta\text{-}\text{lactose}$
- Slow crystallization results in big crystals, whereas fast process leads to formation of small crystals
- Amorphous lactose is formed during rapid drying, which is present in the glassy state and starts to crystallize when moisture content is above certain value (8%);
- Is less sweet than saccharose α (5 times), β (2 times);
- It is hydrolyzed by acids and enzymes (β -D-galactosidase);
- Reacts with amino acids in the Maillard reaction (brown colour, loss of nutritive value, off-flavours).



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Mineral compounds in milk – macroelements (mg/100 mL)

Macroelement	Average content	Range
Calcium	120	100 - 140
Potassium	145	135 – 155
Sodium	50	35 – 60
Magnesium	13	10 – 15
Phosphorus	95	75 — 110
Chlorine	100	80 - 40
Sulphur	10	-
Carbonates (as HCO ₃ -)	20	-



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Vitamins in milk (mg/1 dm³)

Vitamin	Average content	Range
A ₁ (retinol)	0.35	0.04 - 0.84
D ₃ (cholecalciferol)	0.0008	0.00003 - 0.005
E (α -tocopherol)	1.4	0.12 – 1.84
B ₁ (thiamine)	0.43	0.17 – 0.90
B ₂ (riboflavin)	1.7	0.6 – 3.3
B ₆ (pyridoxine)	0.48	0.17 – 1.90
B ₁₂ (cobalamin)	0.0045	0.0008 - 0.018
C (ascorbic acid)	18.0	5.0 - 35.0
H (biotin)	0.04	0.01 – 0.11
Pantothenic acid	3.6	1.5 – 6.6
Nicotinic acid (niacin)	0.95	0.2 – 2.0
Folic acid (folacin)	0.055	0.018 – 0.090



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Milk composition – 3 phases system

- 1. Fat globules oil/water emulsion
- 2. Casein micelles colloidal solution
- 3. Lactose, whey proteins, minerals true solution/ aqueous phase



http://ansci.illinois.edu/static/ansc438/Milkcompsynth/milkcomp_physicochem.html



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Milk physicochemical properties

- Sensory characteristics: homogeneous, opaque liquid, white with light cream shadow, without off-flavours with slightly sweet taste of lactose
- Density: 1.027 1.033 g/cm³
- Viscosity: on average 2-times higher than water
- Surface tension work required to increase the area of a liquid free surface by unit amount –

milk app. 52 mN/m vs. water 72.8 mN/m



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Milk physicochemical properties

- Osmotic pressure constant (isotonic liquid)
- Freezing point: from -0.522 to -0.513°C
- Active acidity (pH): 6.5 6.8
- Titratable acidity: 6.5 7.5°SH
- Buffering capacity capacity to resist pH changes depends on the non-fat dry matter content (proteins, minerals)



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Nutritional value of milk

- Fully valued protein containing all essential amino acids
 - 1 dm³ of milk covers daily human demand for:
 - leucine, isoleucine, lysine, threonine, tryptophan and valine in 100%
 - phenylalanine *in 80%*
 - methionine in 50%
 - Essential amino acids constitute: 45.8% casein and

52.7% in whey proteins



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Nutritional value of milk

- PER (protein efficiency ratio) for case = 2.5; β -Lg = 3.5; α -La = 4.0
- Indexes* for liquid milk:

CS = 63 EAAI = 87 NPU = 83 % TD = 97 %

- Limiting amino acids: methionine and cystine
- Nutritional value comparable to beef and pork protein,
- α -La higher biological value than hen's egg white

* CS – chemical score - the ratio of a gram of the limiting amino acid in a test diet to the same amount of the corresponding amino acid in a reference diet (eg, whole-egg protein) multiplied by 100 (FAO/WHO)
EAAI – essential amino acid index
NPU - net protein utilization – is the ratio of amino acid converted to proteins to the ratio of amino acids supplied
TD – true digestability



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Essential amino acids

• The content of essential and conditionally essential amino acids in milk proteins (mg/g protein) [Tome, 2002]

Amino acid	Total milk protein	Casein	Whey proteins	Alfa-la	FAO 1990 (infants)	FAO 1990 (adults)
Isoleucine	64	57	68	52	56	28
Leucine	104	104	111	98	93	66
Lysine	83	83	99	92	66	58
Methionine and Cysteine	33	31	48	50	42	25
Phenylalanine and Tyrosine	105	111	73	80	72	63
Threonine	51	46	80	52	43	34
Tryptophan	14	14	21	27	17	11
Valine	68	68	68	53	55	35
Histidine	28	29	22	26	26	19



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Essential amino acids

• Actual (real) absorption of essential amino acids (%) in human [Tome, 2002]

	Milk proteins	Soy protein (Isolate)
Total nitrogen	95	91
Histidine	95	92
Isoleucine	95	93
Leucine	95	93
Lysine	95	95
Phenylalanine	96	95
Threonine	93	89
Valine	96	92



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Nutritional value of milk fat

- High digestibility 97 99 %
- High content of the short- and medium-chain FA (fatty acids) 10-15 %
- The content of the essential unsaturated FA (EUFA) app. 2.5 %
- cholesterol 0.1 0.4 % (10 20 mg/100 g milk)
- 14% FA from milk increases cholesterol level in blood
- 45% FA from milk decreases cholesterol level in blood
- 41% FA from milk has no impact on the cholesterol level in blood



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Bioactive milk components – fat fraction

- monoacylglycerols antibacterial and anticancer effect
- phospholipids (sphingomyelins) anticancer effect
- unsaturated fatty acids
 - mono-unsaturated MUFA (oleic c_{18:1})
 - poly-unsaturated PUFA: ω -6 (linoleic c_{18:2}, arachidonic [aa] c_{20:4})

ω-3 (eicosapentaenoic [EPA] c_{20:5})

(docosahexaenoic [DHA] c_{22:6})

- decrease level of total cholesterol and LDL cholesterol
- prevent blood clotting, positive effect on the cardiovascular system
- increase resistance to infections
- retard cancer development
- precursors of eicosanoids: prostaglandins, prostacyclins, tromboxanes and leukotrienes
- Conjugated linoleic acids [CLA]
- β -caroten, Vit. A i E antioxidant and anticancer action



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Nutritional value of lactose

- energy-providing nutrient in neonates ad infants;
- increases bioavailability of vitamin D, calcium, magnesium and phosphorus and some microelements;
- increases peristalsis and growth of lactic acid bacteria in the large intestine - prevention of putrefaction and accelerating the excretion of toxins from the body;
- source of galactose essential for the development and normal function of the nervous system.



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Nutritional value of milk

- rich source of highly bio-available calcium, phosphorus and potassium
- assimilation of calcium from milk 80% (vs. 13% from vegetables) or soy milk)
- calcium in milk is connected with organic proteins (casein micelles – colloidal calcium phosphate)
- favourable molar ratio Ca/phosphorus 1.2 : 1;
- lactose and vit. D_3 enhances calcium bioavailability;
- 1000 cm³ of milk covers daily demand for Ca in 100% (1200 mg);
- 1 dm³ of milk covers daily demand for K in 75 %;
- Base-forming minerals are prevailing in milk important in a • maintenance of the acid-base balance



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Nutritional value of milk

• Vitamins – 1 dm³ of milk covers daily demand for certain vitamins in:

Vitamin	Demand coverage (%)
B ₁₂	100
B ₂	70-110
Folic acid	75
B ₁	33-42
А	25
B ₆	20
Biotin (B ₇)	15-20
С	15
E	10
D	8
niacin	6





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Antioxidant potential of milk

• Enzymatic antioxidant system:

- superoxide dismutase
- catalase
- lactoperoxidase
- glutathione peroxidase (selenium-dependent)



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Antioxidant potential of milk

• Non-enzymatic antioxidants:

- bioactive peptides
- lactoferrin
- vitamin A, E and C
- β-caroten
- coenzyme Q10 (ubiquinone)
- CLA (conjugated linoleic acid)
- glutathione

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Antioxidant potential of milk

- very active lipophilic antioxidant substances;
- high thermal stability of the antioxidants;
- synergism between antioxidants:
 - Co-operation between certain antioxidant substances, which enables regeneration of some compounds to the detriment of the others.
 - Ascorbic acid reduces tocopherol radical to α-tocopherol. Dehydroascorbic acid is reduced to ascorbic acid by the reduced glutathione.
 - High antioxidant potential of milk is a consequence of the synergistic interactions between lipophilic and hydrophilic antioxidants.



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Milk – nutritional failures

- Alergenic properties of milk proteins
 - β -lactoglobulin 62% (not present in human milk)
 - casein 60%
 - α- lactalbumin 53%
 - Blood serum albumin 52%
 - Products of protein digestion
 - In Poland 2.7% of non-breast-fed (formula-fed) and 1.8% of breastfed infants suffer from allergy to cow's milk proteins (in 90% of them allergy will stop before 5th birthday)



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Milk – nutritional failures

- Lactose intolerance lack of or too low activity of the β-Dgalactosidase (lactase) enzyme
- Galactose intolerance (galactosemia*)
- Milk anemia consumption by infants and young children milk without supplementation with food rich in iron and vitamin C

* Galactosemia is an inability to properly break down galactose due to a genetically inherited mutation in one of the enzymes



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Thank you for your attention

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